

## CHEM-E4205 (5 cr):

### Crystallography Basics & Structural Characterization

The course deals with **crystal chemistry** concepts and structural **characterization** techniques of **inorganic materials** and covers also the basics of **crystallography**. The emphases are on the various diffraction and spectroscopic methods used for phase identification, **crystal structure** determination and studies of **chemical environment**.

Time Slots	Tuesday 12–14, Friday 10-12 & Friday 14–16
Lectures	Lectures in Zoom; lecture slides and additional reference material (if needed) provided in MyCourses before the start of each lecture.
Exercises	Last part of Friday hours (Zoom or Classroom D422): to explain the assignments & give some guiding. Exercise answers returned by next Monday 6 pm.
Seminars	Given individually on an assigned topic
Teachers:	Maarit Karppinen Eeva Rautama (Rietveld) Sami Vasala (Synchrotron & XAS & RIXS) Ramin Ghiyasi (XRR)

# SCHEDULE

	Date	Topic
1.	Tue 14.09.	Lec-1: Introduction
2.	Fri 17.09.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Fri 17.09.	<b>EXERCISE 1</b>
4.	Tue 21.09.	Lec-3: Crystal Chemistry & BVS
5.	Fri 24.09.	Lec-4: Symmetry & Point Groups
6.	Fri 24.09.	<b>EXERCISE 2</b>
7.	Tue 28.10.	Lec-5: Crystallography & Space Groups
8.	Fri 01.10.	Lec-6: XRD & Reciprocal lattice
9.	Fri 01.10.	<b>EXERCISE 3</b>
10.	Tue 05.10.	Lec-7: ND & GI-XRD
11.	Fri 08.10.	Lec-8: Rietveld
12.	Fri 08.10	<b>EXERCISE 4: Rietveld</b>
13.	Tue 12.10.	Lec-9: Synchrotron radiation & XAS & RIXS
14.	Fri 15.10.	Lec-10: EXAFS & Mössbauer
15.	Fri 15.10.	<b>EXERCISE 5</b>
16.	Tue 19.10.	Seminars: XPS, FTIR, Raman, ED, HRTEM, SEM, AFM
17.	Fri 19.10.	Lec-11: XRR
18.	Fri 22.10.	<b>EXERCISE 6: XRR</b>

COURSE START:  
Tue 14.09. at 12.15  
in Zoom

**EXAM:**  
**Fri Oct. 29, 2021**

## **GRADING (max 100 points)**

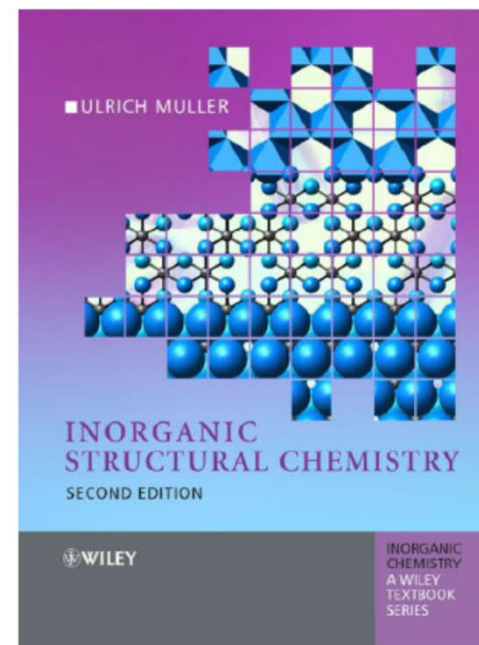
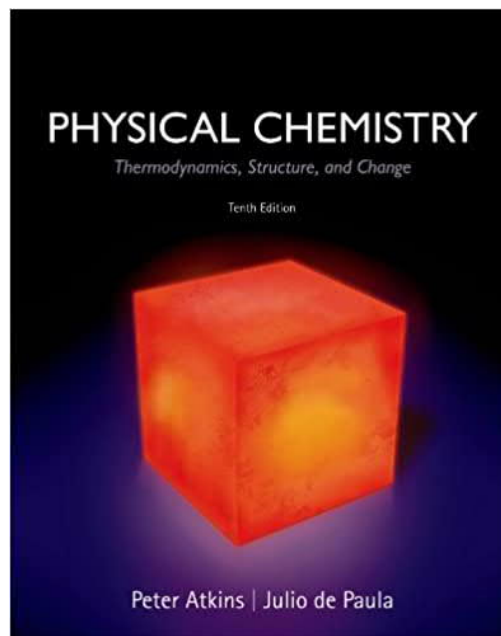
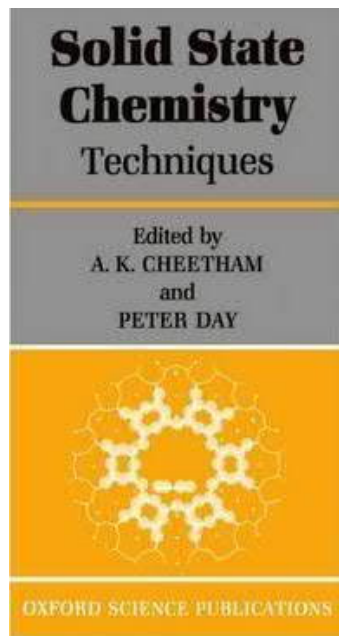
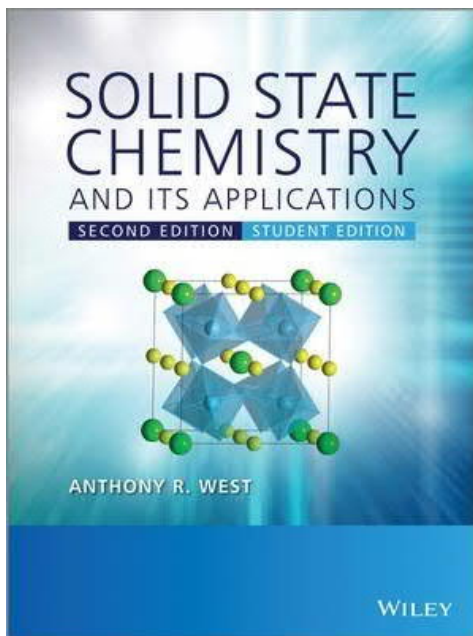
- Exam: 0 – 44 points
- Exercises: = 0 – 36 (= 6 x 6) points
- Seminar (mandatory): 10 – 20 points

# INSTRUCTIONS for SEMINAR PRESENTATION/REPORT

- Topics: **IR, Raman, XPS, SEM, AFM, HRTEM, ED, EELS**
- Seminar presentation is mandatory
- Given individually
- Evaluated in the scale: 10 ~ 20 points
- Presentation is given in English, and the slides will be put up in MyCourses afterwards
- Presentation: 25+5 minutes
- Rough content of the presentation/report:
  - principle of the technique
  - type of information gained
  - interpretation of the measured data
  - pros & cons
  - **two to three research examples**  
(you will be given some relevant research papers for an example)

# TEXT BOOKs & Background Knowledge

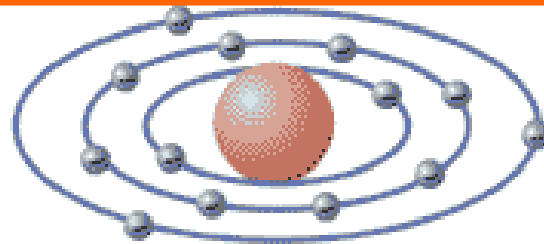
- ❖ This course does not follow any specific text book; no text book fully covers the topics included; below are examples of text books which could be useful reference/background books for many of the course topics.
- ❖ Although the following two courses are not mandatory prerequisites, it may be difficult to follow this course without a similar basic background knowledge on inorganic (materials) chemistry and solid state chemistry:
- ❖ CHEM-E4130: Chemistry of Elements (Maarit Karppinen)
- ❖ CHEM-E4155: Solid State Chemistry (Antti Karttunen)



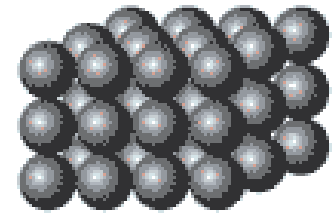
# Structure of materials (in different levels)

- (a) Single atom: electron/spin configuration => valence/oxidation state & spin state
- (+) Local structure: bonding structure/coordination sphere
- (b) Crystal structure: (periodic) locations of different atoms in regular crystal lattice
- (+) Magnetic structure (periodic) ordering of spins
- (c) Microstructure: e.g. particle size/shape, grain boundaries
- (d) Phase/macroscale structure

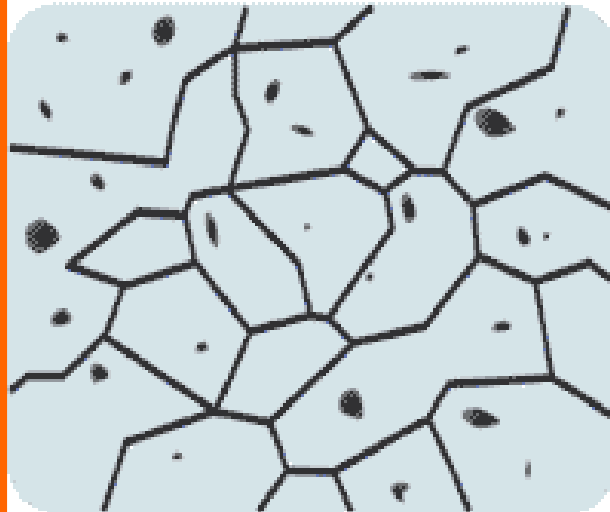
**All these levels of material's structure significantly affect the material's properties**



(a)



(b)



(c)



(d)

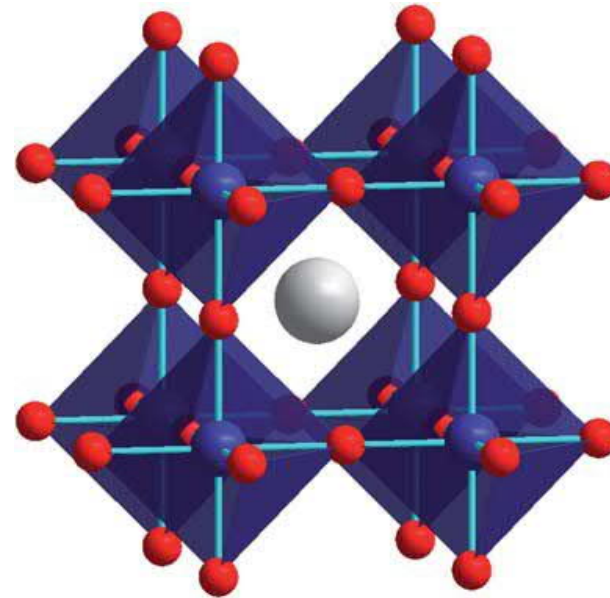
# LECTURE 1: INTRODUCTION

The course deals with structural characterization techniques of inorganic materials and covers also the basics of crystallography. The emphases are on the various diffraction and spectroscopic methods used for phase identification, **crystal structure** determination and studies of **chemical environment**.

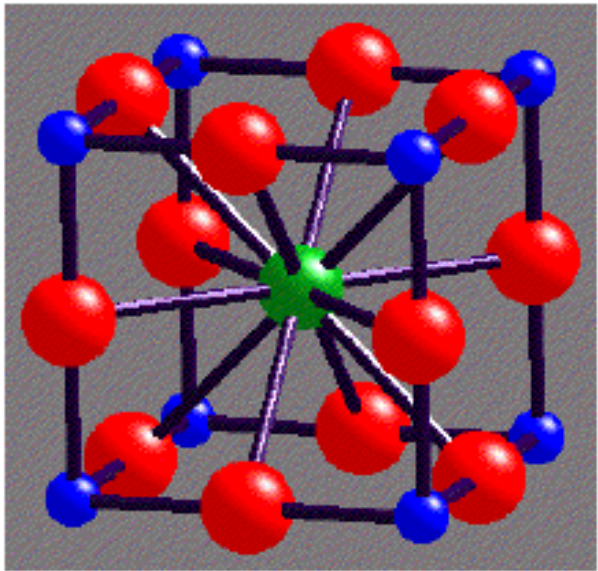
- Important: relations between crystal structure, chemical environment (coordination and valence) and material properties
- To get the full picture, a wide arsenal of different characterization techniques are needed for: crystal structure (XRD, ND, ED, HRTEM, EXAFS, RIXS), morphology (SEM, TEM, AFM), chemical environment (EXAFS, XANES, Mössbauer, XPS, IR, Raman) and properties (e.g. ND, Mössbauer for magnetic properties)
- Information needed in particular for: small distortions, different defects (vacancy, interstitial, antisite, etc.), mixed metal valences, magnetic structures, etc.
- For thin film characterization, specific techniques are needed (GIXRD, XRR)
- **Perovskite structure** is often used as a model/example case; however, all the issues discussed in the context of the perovskite structure are directly transferable to many other inorganic materials

# (Inorganic) PEROVSKITE $ABO_3$

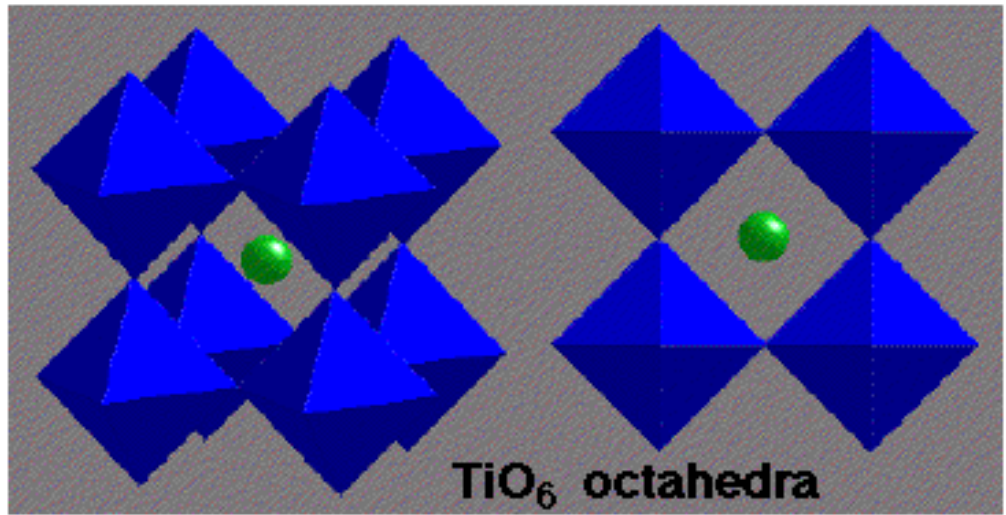
- Thousands of perovskite compounds known
- Structure named after the mineral Perovskite  $CaTiO_3$
- Mineral found in Ural Mountains, named in 1839 after Russian mineralogist, Von Perovski
- Components: - **A**: large metal
  - **B**: small (transition) metal
  - **O**: oxygen (can also be halogen)
- Oxygen deficiency (very common):  $ABO_{3-\delta}$
- Because of these possibilities of chemical composition tuning, perovskite compounds can be tailored to a wide variety of functional properties
- Ideal perovskite has cubic unit cell; coordination numbers:  $CN(A)=12$ ,  $CN(B)=6$ ,  $CN(O)=6$
- Valences:  $V(A) + V(B) = 6$ ,  
e.g.  $La^{III}Sc^{III}O_3$ ,  $Sr^{II}Ti^{IV}O_3$ ,  $Na^{I}Nb^{V}O_3$
- Tuning the chemical composition controls redox chemistry (metal valences) and tiny crystal structure distortions (in CNs, bond lengths, bond angles)
- Metal valences and structural distortions control the functional properties







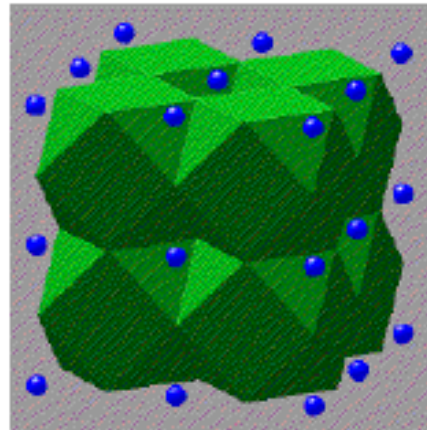
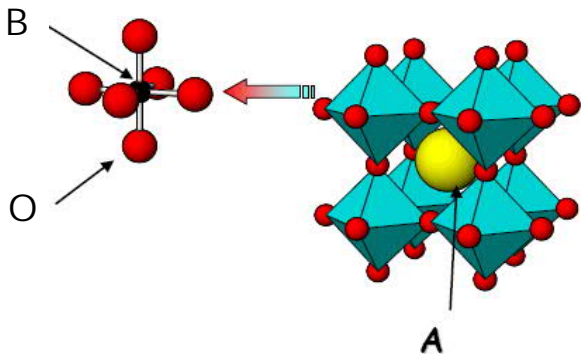
A-Cell



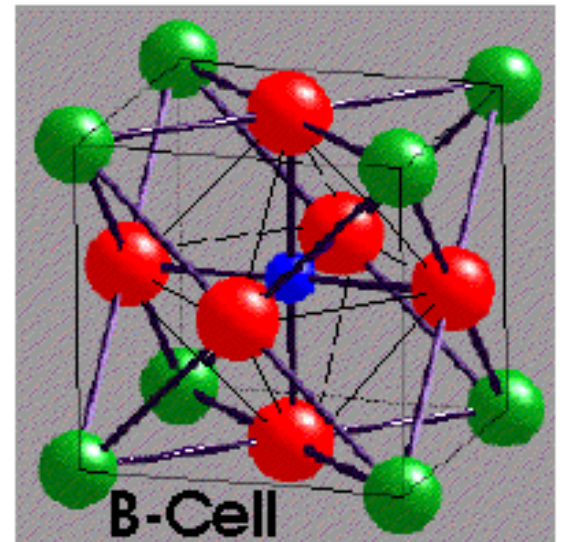
TiO<sub>6</sub> octahedra

# Perovskite CaTiO<sub>3</sub>

● Ca ● Ti ● O



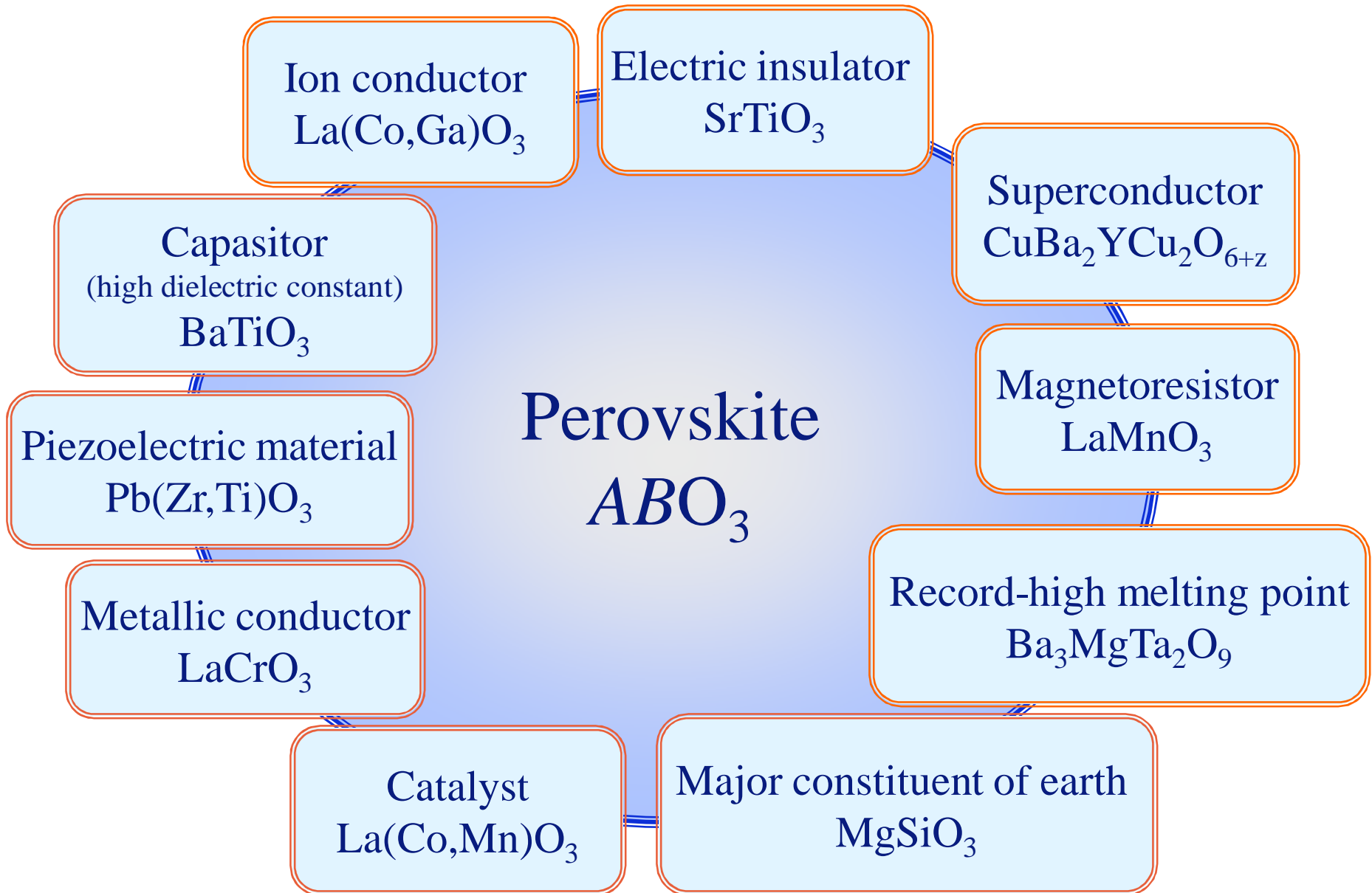
CaO<sub>12</sub> cuboctahedra



B-Cell

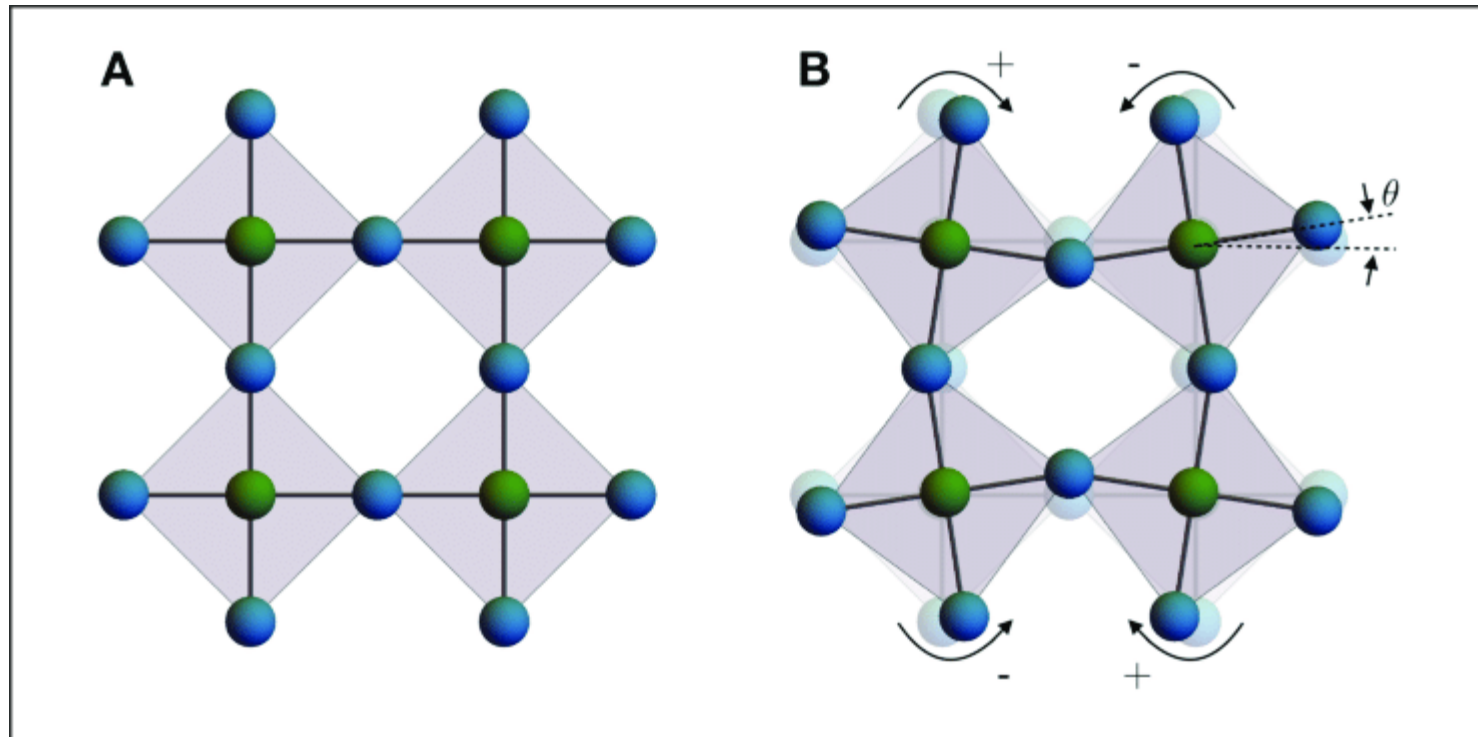
Different presentations of the perovskite structure

# Perovskite – Multifunctional structure



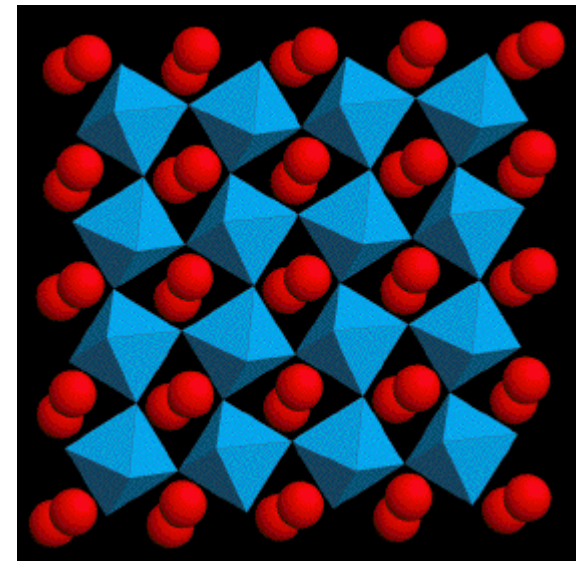
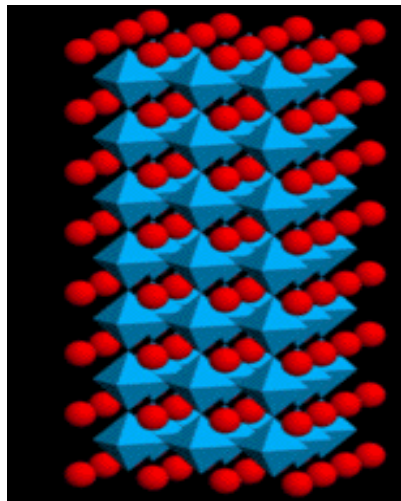
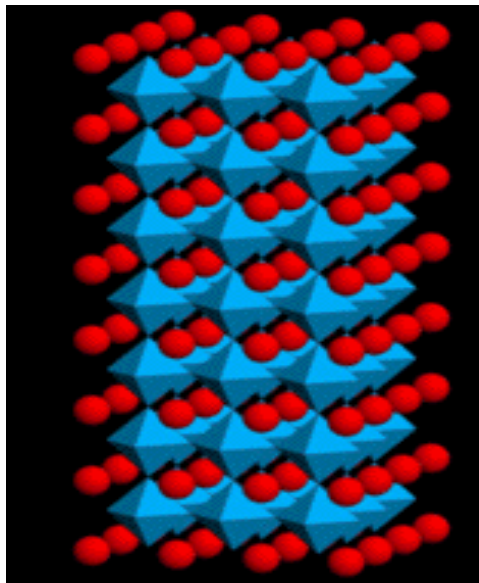
# COMMON EXAMPLE OF DISTORTIONS in $ABO_3$

- Oxygen atoms often move from their ideal positions such that the  $BO_6$  octahedra e.g. get tilted
- There are many other ways for oxygen atoms to get displaced
- These **distortions affect many properties** (magnetic, ferroelectric, etc.)



# HYPOTHETICAL EXAMPLE: Ferromagnetic (Ba/Sr/Ca)BO<sub>3</sub>

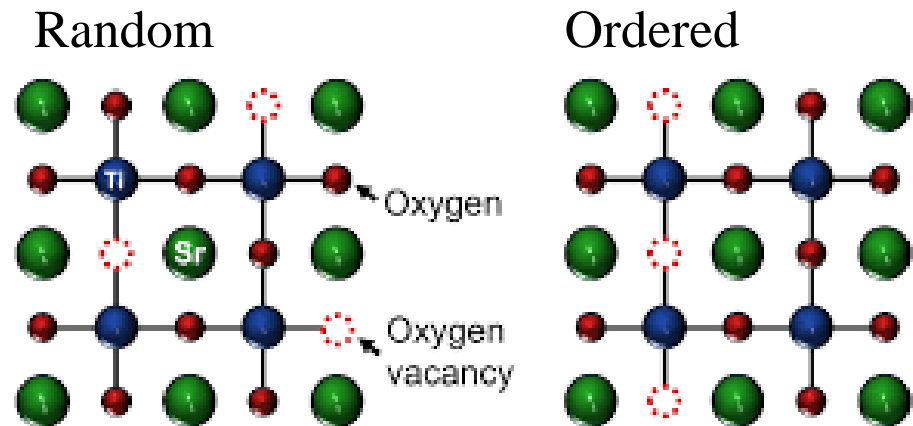
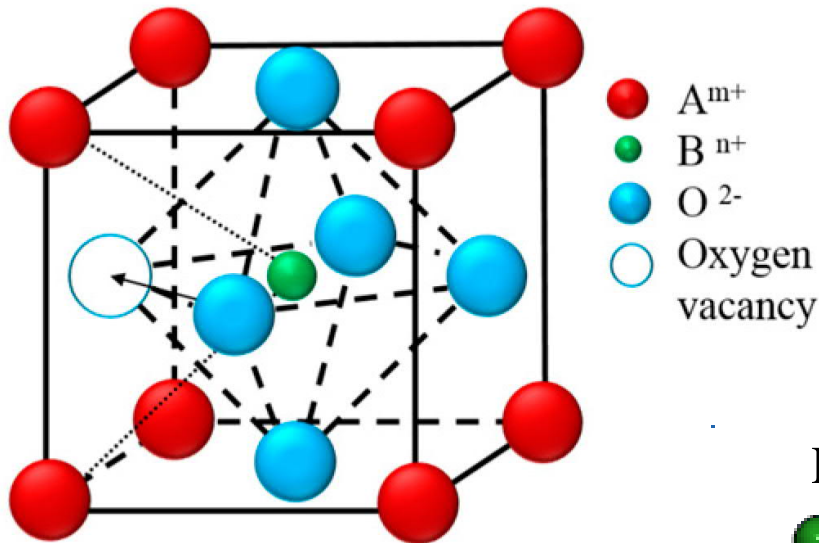
- Ferromagnetic transition temperature ( $T_C$ ) highest when strong B-O-B interactions: short bond length and non-tilted bonding
- LEFT: with the largest  $A = \text{Ba}$  cation, ideal perovskite structure, **B-O-B** bond angle 180 °C, but **B-O** bond length long  $\rightarrow T_C = 320 \text{ K}$
- MIDDLE: with the intermediate-sized  $A = \text{Sr}$  cation, ideal perovskite structure, **B-O-B** bond angle 180 °C, and **B-O** bond length shorter  $\rightarrow T_C = 400 \text{ K}$
- RIGHT: with the smallest  $A = \text{Ca}$  cation, tilted perovskite structure, **B-O** bond length short, but the **B-O-B** bond angle  $< 180$  °C  $\rightarrow T_C = 370 \text{ K}$





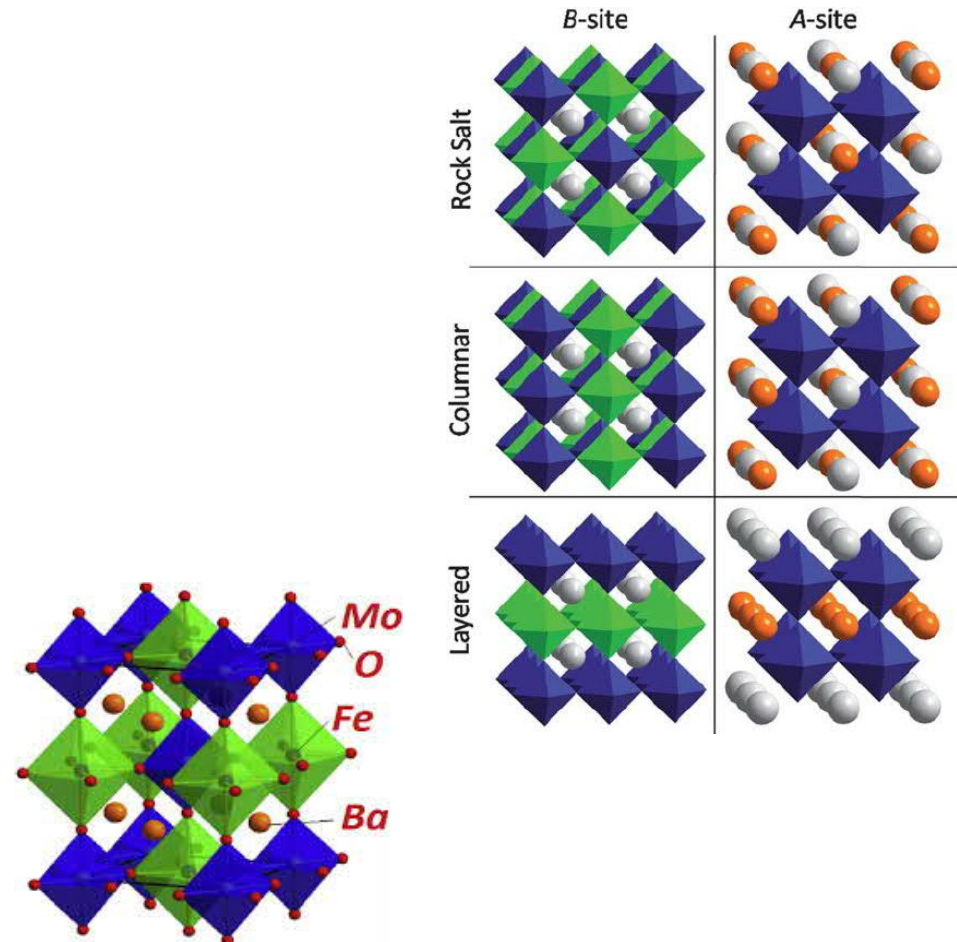
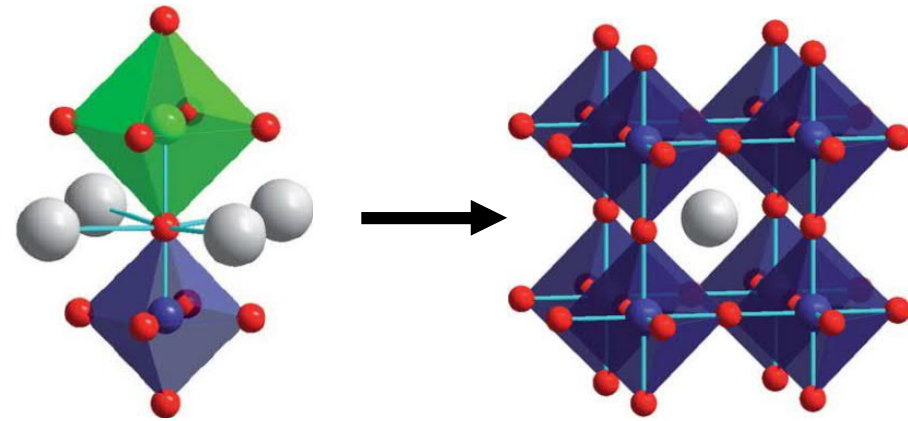
# OXYGEN DEFICIENCY in $ABO_{3-\delta}$

- Oxygen nonstoichiometry, even within the wide range of  $0 < \delta < 0.5$ , is very common among perovskite compounds
- **Oxygen content controls the metal valences and thereby the properties**
- Oxygen vacancies can be randomly located or ordered along different patterns



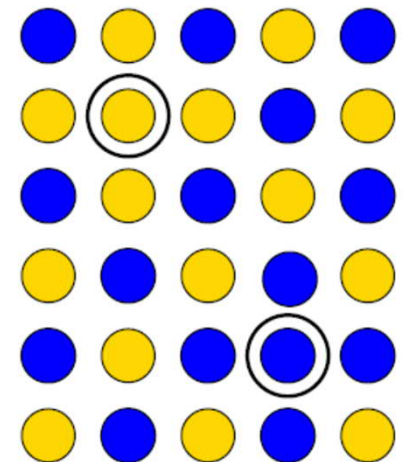
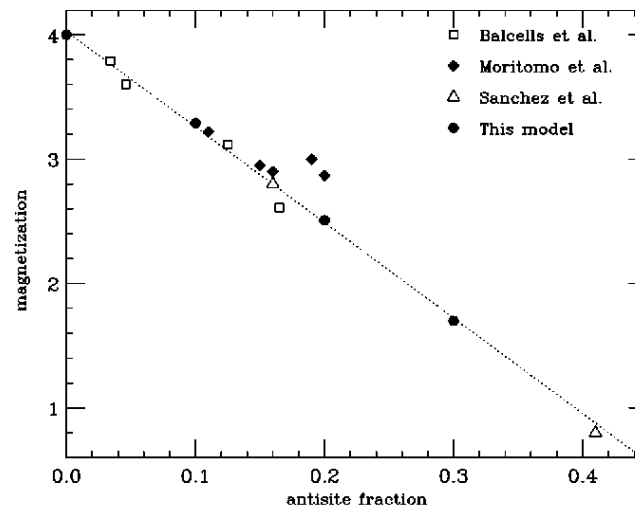
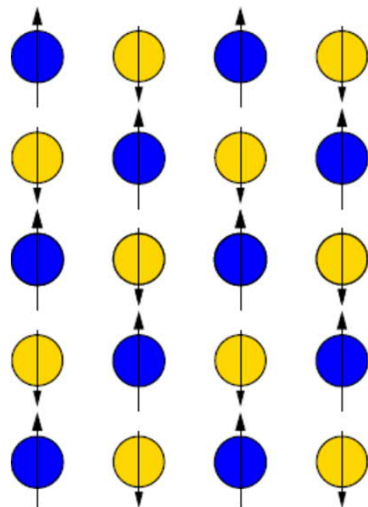
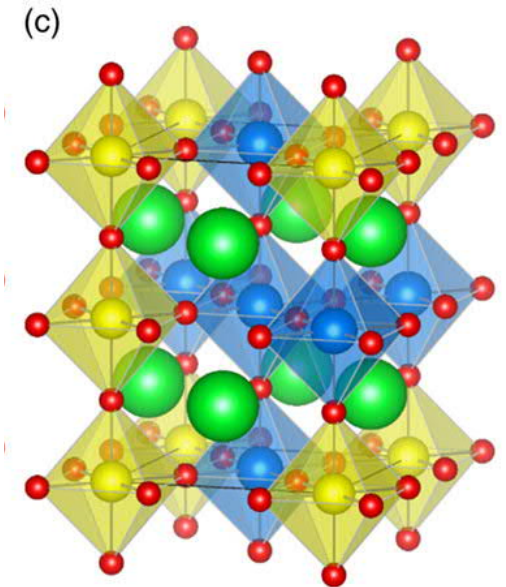
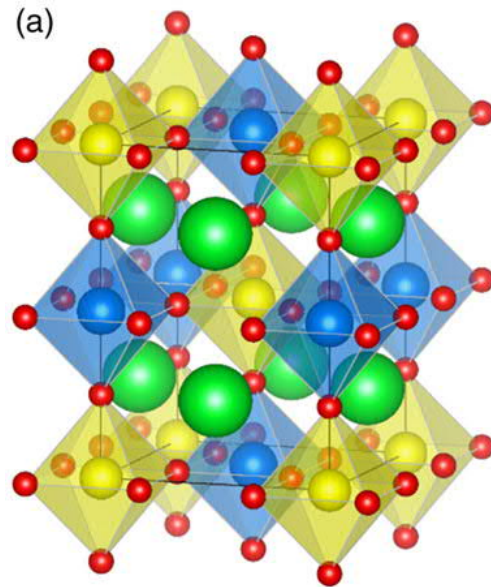
# DOUBLE PEROVSKITES

- Two different cations (**B'** and **B''**) occupy the B-site with 50%/50% ratio and in an ordered manner → B-site ordered double perovskite
- Two different cations (**A'** and **A''**) occupy the A-site with the 50%/50% ratio and in an ordered manner → A-site ordered double perovskite
- For both cases, there are multiple different ordering patterns
- Many double perovskite compounds show exciting functional properties, e.g. the B-site ordered halfmetallic  $\text{Sr}_2\text{FeMoO}_6$  (simultaneously ferromagnetic and electrically conducting → magnetic-field control of conductivity → spintronics)



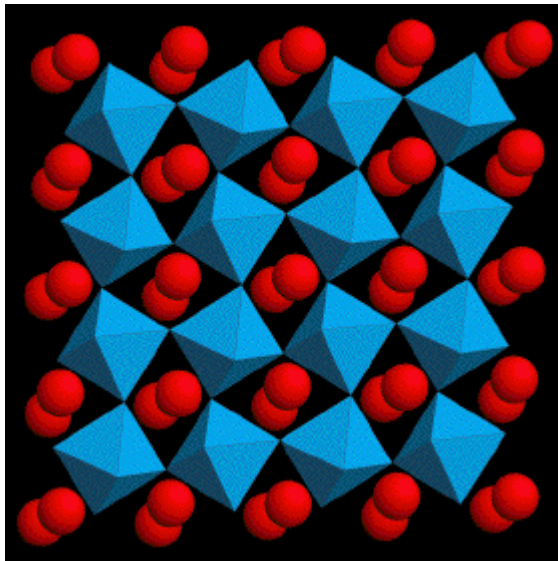
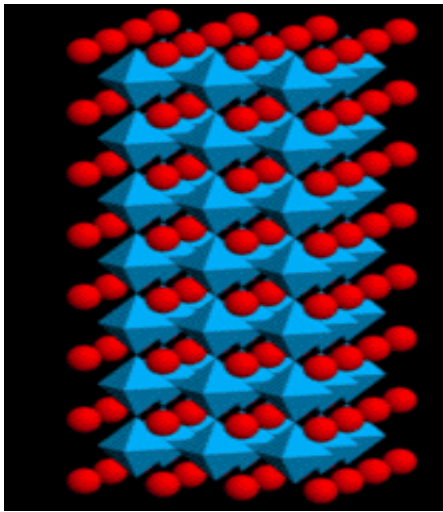
# ANTISITE DEFECTS in $A_2B'B''O_6$

- Ordering of  $B'$  and  $B''$  is not always perfect
- Antisite (=defected) atom is  $B'$  cation at the  $B''$  site, and vice versa

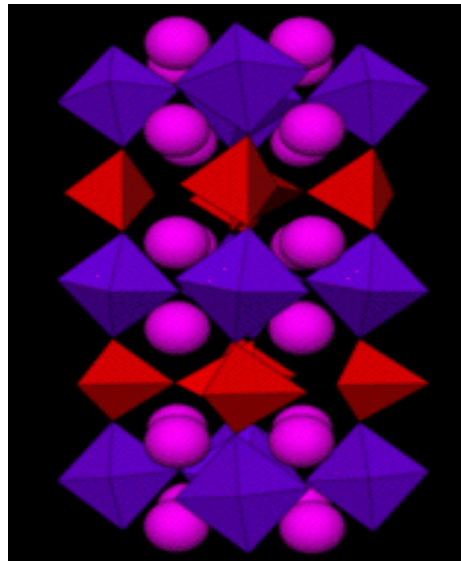


# “Distortions and Imperfections” in Perovskite Structure

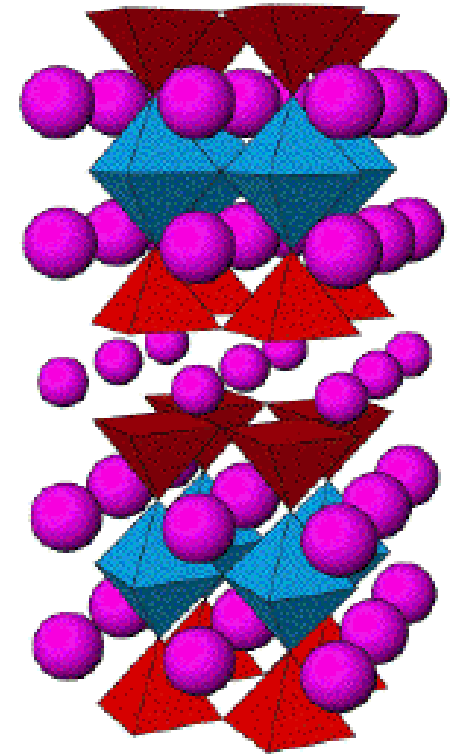
- often the source of the desired properties



Changes in  
atomic positions



Oxygen deficiency

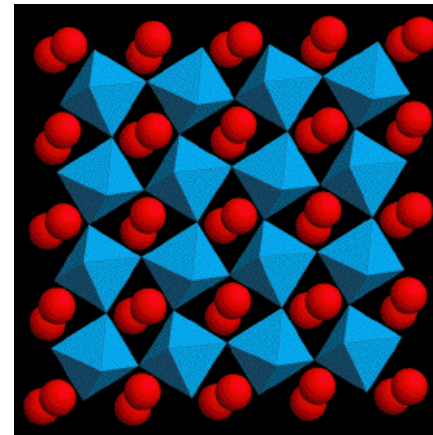
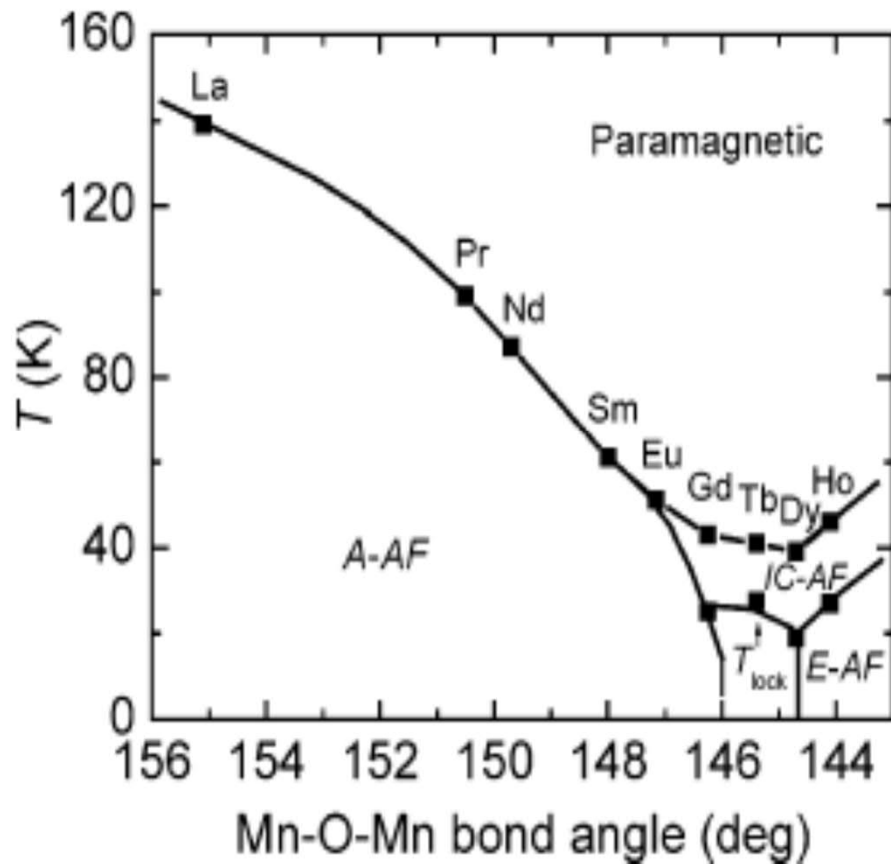


Ordering of cations  
→ Layered structure



# ANTIFERROMAGNETIC (AF) $\text{LnMnO}_3$ PEROVSKITES

- Magnetic transition temperature increases with:
  - decreasing Mn-O-Mn bond length
  - increasing Mn-O-Mn bond angle (closer to  $180^\circ$ )



Y.H. Huang, H. Fjellvåg, M. Karppinen, B.C. Hauback, H. Yamauchi & J.B. Goodenough, *Chem. Mater.* **18**, 2130 (2006).

- **The International Union of Crystallography (IUCr):** <https://www.iucr.org/>
- A crystallography promo video from IUCr:  
<https://www.youtube.com/watch?v=m2maeeA9z84&list>
- Very nice introduction to crystallography:  
<http://www.xtal.iqfr.csic.es/Cristalografia/cascara-en.html>
- **The Crystallography Open Database** <http://www.crystallography.net/cod/>
- **Vesta** a small but very nice program to depict crystal structures (e.g. load .cif files from the database and look at them with vesta): <http://jp-minerals.org/vesta/en/>